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Synthesis and Spectroscopic Characterisation of Bis[bis(Bipyridine)ruthenium(II)]-3,3',4,4'-Tetraiminobiphenyl and its Redox Products

By

P.R. Auburn and A.B.P. Lever*

in
Inorganic Chemistry



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"Synthesis and Spectroscopic Characterisation of
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and its Redox Products"

Pamela R. Auburn and A.B.P.Lever*

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Abstract (Not for inclusion in Communication)

3,3',4,4'-Tetraiminobiphenyl forms a redox series of binuclear complexes obtained by coordinating the Ru(bpy)₂ [bpy = 2,2'-bipyridine] fragment at each end of the molecule. The ligand is capable of existing in six redox states, and three of these, including a mixed valence species, are characterised as their bis[Ru(bpy)₂] complexes. Electrochemical, electron spin resonance and optical data are presented. These are discussed in terms of localisation and delocalisation of the ruthenium to ligand charge transfer states as a function of redox level. The mixed valence species displays an inter-valence (ligand to ligand) charge transfer band, and the degree of electronic coupling is shown to be relatively large. There is some evidence that the biphenyl twist angle changes with oxidation state suggesting that these complexes might be useful building blocks for molecular wires and switches.

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"Synthesis and Spectroscopic Characterisation of
Bis[bis(Bipyridine)ruthenium(II)]-3,3',4,4'-Tetraiminobiphenyl
and its Redox Products"

Pamela R. Auburn and A.B.P. Lever*

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Our recent studies with ruthenium dioxolene species¹⁻⁵ have emphasized the extensive mixing between the ruthenium d orbitals and the dioxolene ligand molecular orbitals, mixing which can be tuned by altering the oxidation state of the complex. We report ruthenium complexes of 3,3',4,4'-tetraaminobiphenyl, forming dinuclear species, in a redox series, three members of which are described. The formation of conduction bands through polymeric versions of these complexes might allow for the construction of molecular wires which could be switched by altering the oxidation state, which will alter the degree of conjugation in the pathway⁶, and/or control the angle of twist at the biphenyl ligand.

Much is known of electron transfer between two metals of different oxidation state via a bridging ligand⁷⁻⁹. Less is known of electron transfer between ligands of different oxidation state.¹⁰⁻¹²

4 $[\text{Ru(II)(bpy)}_{22}-3,3',4,4'\text{-tetraiminobiphenyl}](\text{PF}_6)_4$ (bpy = 2,2'-bipyridine)^{13,14} isolated in this bis(quinonediimine) oxidation level is abbreviated (RuQ, QRu). The labels Q, SQ and CAT refer to the successively reduced quinonediimine fragment. A mononuclear $[\text{Ru(II)(bpy)}_2]-3,4\text{-diimino-}3',4'\text{-diamino biphenyl}](\text{PF}_6)_2$ species (RuQ, CAT) was also isolated¹⁵.

Using studies of related mononuclear ruthenium quinonoid¹⁻⁴ and quinonediimine⁵ species, the electronic spectra (Fig.1) are assigned (Table 1). Charge transfer

transitions occur from ruthenium to bipyridine and to the quinonediimine ligands in the spectra of both complexes (RuQ,QRu)¹⁶ and (RuQ,CAT). The oscillator strength of the Ru(II)---> π^* Q transition in the dinuclear species is almost twice that in the mononuclear species but the Ru(II)---> π^* transition is substantially more narrow in the (RuQ,QRu) complex. This narrowness is indicative of a smaller reorganisation contribution, and hence less charge transfer character in the excited state of (RuQ,QRu), than in (RuQ,CAT). Evidently the excited electron is spread over both quinonediimine fragments in this symmetric albeit not strictly co-planar biphenyl di-ligand¹⁷. This species does not emit in fluid medium at room temperature probably a consequence of internal redox quenching between the Ru---> π^* (bpy) MLCT state and the quinonediimine fragment.

Voltammetry of (RuQ,QRu) in acetonitriles show two oxidation processes at 1.39V and 1.51V (vs AgCl/Ag in CH₃CN) assigned to the formation of (Ru(III)(Q...Q)Ru(II)) and (Ru(III)(Q...Q)Ru(III)) respectively. There are four successive reductions of the biphenyl ligand (Fig.2) (-0.27, -0.49, -1.11 and -1.25V vs AgCl/Ag) illustrating a series of mixed valence products. Two more negative processes (at -1.56 and -1.70V) correspond with bipyridine reductions. The mononuclear species (RuQ,CAT) has two reduction processes generating (RuSQ,CAT) and (RuCAT,CAT) in acetonitrile at -0.485 and -1.12V vs AgCl/C₁, respectively.

Controlled potential reduction of (RuQ,QRu) in propylene carbonate, just negative of the first and second reduction couples yields, respectively, (RuQ,SQRu), which may also be generated chemically by triethylamine reduction of (RuQ,QRu), and is stable indefinitely and (RuSQ,SQRu) which shows slow decomposition which could not be overcome regardless of solvent.

Species (RuQ,SQRu) shows a free radical esr spectrum ($g = 2.00$, $\Delta_{pp} = 19$ gauss, no hyperfine coupling to nitrogen, at 77K)⁷ while (RuSQ,SQRu) is esr silent at least to liquid nitrogen temperature. The electron in (RuQ,SQRu) is evidently ligand localised and the electronic structure is clearly different from the analog-

gous (NH_3); Ru(II)-(1,4-diiminobenzene)-Ru(III)(NH_3); species with a metal localised esr spectrum¹⁸.

(RuQ,SQRu) shows the Ru(II) $\rightarrow \pi^*(1)$ bipy electronic transition shifted to lower energy relative to (RuQ,QRu) since the overall positive charge on the ruthenium centres has been decreased. A Ru(II) $\rightarrow \pi^* Q$ transition appears at essentially the same energy as that of the monomeric (RuQ,CAT) species. The Ru(II) $\rightarrow \pi^* SQ$ transition, at $12,900 \text{ cm}^{-1}$, is shifted to the red of that observed in monomeric (RuSQ,CAT) but is substantially broader and more intense (Fig.3)(Table 1). The higher energy shoulder on this band may arise through splitting in the t_{2g} manifold, or is perhaps an internal ligand transition. It lies fortuitously at almost the same energy as the Ru $\rightarrow \pi^* (SQ)$ transition in mononuclear (RuSQ,CAT). However the possibility that this mononuclear species is an impurity in the dinuclear (RuQ,SQRu) is eliminated by NMR spectroscopy. An additional broad transition at 7750 cm^{-1} , in (RuQ,SQRu) is absent from the spectrum of the mononuclear (RuSQ,CAT) and lies at too low an energy¹ to be regarded as an MLCT Ru(II) \rightarrow SQ type transition.

(RuQ,SQRu) may exist in two extreme forms, (1a), where the two ligating termini are electronically and structurally equivalent existing midway between Q and SQ, and (1b), where the SQ and Q termini are distinct, differing electronically and structurally, likely caused by twisting at the central C-C bond¹⁷.

The electronic spectra appear to support (1b) albeit with some electronic coupling between the two ends of the molecule. The band at 7750 cm^{-1} is then regarded as an intervalence LLCT (ligand-to-ligand charge transfer state, though in this case more an intramolecular LLCT) transition. This intervalence band is broad (half-bandwidth ca 2050 cm^{-1}) as a consequence of a significant re-organisation contribution. The delocalisation coefficient⁹ $\alpha^2 = 1.1/R^2 = 0.05$, if the inter-ligand distance, R, is assumed to be that between the centres of the two benzene rings, ca 4.5 Å. The appropriate value of R to use, is, however, uncertain. The

electron coupling integral is estimated^{9,19} to lie in the range 0.2-0.35 eV (using eqn.25 or 28 in ref.¹⁹) substantially larger than in the Creutz-Taube mixed valence (metal to metal) systems^{10,19} but comparable to the values observed in the shortest M_2N -4-DCV organic systems (dimethoxynaphthalene-dicyanovinyl) discussed by Penfield et al.¹². Thermal electron transfer in this extreme model, will then be extremely fast. This transition is solvent dependent showing a linear dependence upon $[(1/D_{op}) - (1/D_s)]^{9,11}$ with slope 1060 cm^{-1} , intercept 7200 cm^{-1} ($R = 0.996$, 5 solvents)²⁰.

The $\text{Ru(II)} \rightarrow \pi^*$ SQ transition is broader in $(\text{RuQ}, \text{SQRu})$ than in $(\text{RuSQ}, \text{CAT})$ an observation inconsistent with model (1a), but consistent with (1b) especially if the excited state twist angle differs significantly from the ground state. Thus $(\text{RuQ}, \text{SQRu})$ is a Class II²¹ delocalised complex in which the $(\text{bpy})_2\text{Ru(II)}(\text{Q}..)$ and $(\text{bpy})_2\text{Ru(II)}(\text{SQ}..)$ chromophores can separately be identified spectroscopically but which are significantly coupled.

The second reduced species $(\text{RuSQ}, \text{SQRu})$ shows a further red shift in the $\text{Ru(II)} \rightarrow \pi^*(1)(\text{bpy})$, and $\pi^*(2)(\text{bpy})$ transitions relative to $(\text{RuQ}, \text{SQRu})$. The $\text{Ru(II)} \rightarrow \pi^*$ SQ transition does not shift significantly, relative to $(\text{RuQ}, \text{SQRu})$ but it does become weaker and broader; its oscillator strength is probably little changed (Fig.3). A nir band is still observed, shifted to the blue, narrower and more intense than that observed in the spectrum of $(\text{RuQ}, \text{SQRu})$.

The decrease in molar intensity for the $\text{Ru(II)} \rightarrow \pi^*$ MLCT transition is especially informative. If the two halves of the molecule were independent and uncoupled, the oscillator strength of this transition might double relative to the $(\text{RuQ}, \text{SQRu})$ species, since the transition probability doubles.

Consider however that the two π^* orbitals on each SQ terminus couple to yield a lower energy orbital of odd parity which is filled and an upper empty orbital of even parity. The $\text{Ru(II)} \rightarrow \pi^*$ MLCT transitions terminate on this upper orbital. Coupling of the pairs of ruthenium xz, xy and yz orbitals yields three pairs of

orbitals of even and of odd parity. Transitions from the odd parity combinations to the empty ligand orbital generate three possible transitions, one strongly allowed, one weakly allowed and one forbidden. There is therefore one strongly allowed transition per (strongly coupled, delocalised) dinuclear molecule, rather than the two expected in a localised dinuclear molecule; thus the transition probability may not increase relative to (RuQ,SQRu), as observed.

The near infrared absorption has a quite different shape in (RuSQ,SQRu), being narrower (half-bandwidth ca 1500 cm⁻¹) indicative of a smaller difference between the equilibrium ground and excited state potential surfaces, than for (RuQ,SQRu). This is also consistent with a delocalised species with this transition being internal to the (RuSQ,SQRu) framework with little charge transfer character. It is possibly a transition between the pair of SQ terminus molecular orbitals defined in the previous paragraph. Solvent dependence data are not yet available.

Further studies on this system are planned to probe the twist angles both in the ground and excited state, and the variation in coupling between the two termini of the ligand as a function of oxidation state.

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Table 1 Electronic Spectra and Assignments

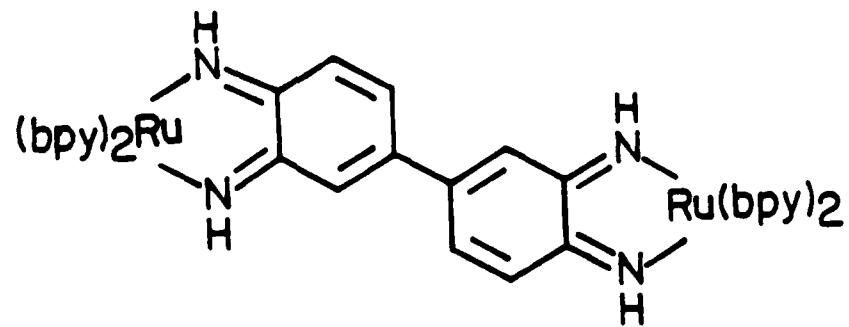
Energy(Log _e)		$\Delta_{1/2}^a$	f ^a	Assignment
(RuQ,QRu) ^b	23,050(4.07)			Ru(II) d--> π^* (1) bpy
	17,100(4.78)	1800	0.5	Ru(II) d---> π^* Q
(RuQ,CAT) ^c	23,000(3.78)			Ru(II) d---> π^* (1) bpy
	19,700sh			
	17,000(4.29)	3930	<0.35 ^d	Ru(II) d---> π^* Q
(RuQ,SQRu) ^b	29,400(4.38)			Ru(II) d---> π^* (2) bpy (?)
	21,500sh			Ru(II) d---> π^* (1) bpy
	18,800(4.33)			Ru(II) d---> π^* Q
	14,800(4.23)			
	12,900(4.28)	2600 ^e	0.23 ^a	Ru(II) d---> π^* SQ
	7,750(4.02)	2050	0.1	SQ --- Q LLCT
(RuSQ,CAT) ^c	23,000(3.94)			
	20,050(4.02)			Ru(II) d---> π^* (1) bpy
	15,300(4.12)	1820	0.11	Ru(II) d---> π^* SQ
(RuSQ,SQRu) ^b	25,400sh			Ru(II) d---> π^* (2) bpy
	18,600(4.23)			Ru(II) d---> π^* (1) bpy
	14,600			
	12,800(4.24)			Ru(II) d---> π^* SQ
	8,500(4.37)	1650	0.18	internal ligand (RuSQ,SQRu)

a) $\Delta_{1/2}$ is the half-bandwidth in wavenumbers, f is the oscillator strength. b)

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in Propylene carbonate. c) in acetonitrile. d) Estimated and likely slightly high due to overlapping bands.



(RuQ,QRu)

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Figure Legends

Fig.1 The electronic spectra of dinuclear (RuQ,QRu) in propylene carbonate with the spectrum of mononuclear (RuQ,CAT) in acetonitrile for comparison.

Fig.2 The differential pulse voltammetry of (RuQ,QRu) in acetonitrile containing tetrabutylammonium hexafluorophosphate as supporting electrolyte. Scan rate 2mV/s; amplitude 5mV.

Fig.3 Electronic spectra of (RuSQ,SQRu) (upper) and (RuQ,SQRu) (lower) in propylene carbonate. The spectrum of mononuclear (RuSQ,CAT) (lower), in acetonitrile, is included for comparison.

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13. {[Ru(bpy)₂-3,3',4,4'-tetraiminobiphenyl](PF₆)₄ (1) (bpy = 2, 2'-bipyridine) (RuQ, QRu)}, was prepared by refluxing Ru(bpy)₂Cl₂ (0.2g) and 3,3'-4,4'-tetraaminobiphenyl (0.044g, Aldrich) in degassed methanol (25mL) for 6h. After cooling to ambient temperature, several drops of concentrated ammonia, and a solution of ammonium hexafluorophosphate (0.2g) in water (2mL) were added. The blood red solution was oxygenated for 45 min. to develop a rich purple color. After solvent removal and trituration with methylene dichloride to remove a red impurity, the product was recrystall-

lised from acetone.

14. ^1H NMR: 12.08(2H, singlet imine); 11.98 (2H, singlet, imine); 8.50 (8H, multiplet); 8.14 (8H, multiplet); 7.62 (8H, multiplet); 7.5 (10H, multiplet), 7.38 (2H, doublet); 7.27 (2H, doublet). Analysis, Calcd. for $\text{C}_{32}\text{H}_{42}\text{F}_{24}\text{N}_{12}\text{P}_4\text{Ru}_2$, C, 38.7; H, 2.6; N, 10.4%. Found, C, 39.2; H, 3.2; N, 9.9.
15. $\{\text{Ru}(\text{bpy})_2-(3,4,-\text{diamino}-3',4'-\text{diiminobiphenyl})\}(\text{PF}_6)_2$. (RuQ, CAT) (bpy=2,2'-bipyridine): $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (0.1g) and 3,3'-diaminobenzidine (0.088g) were refluxed in degassed methanol (25mL) for 24h. The red-orange solution was exposed to air and filtered. The addition of several drops of concentrated ammonia changed the colour to deep blue purple. This solution was oxygenated for 6h and then reduced in volume to 5mL. Dropwise addition of an aqueous saturated soln of NH_4PF_6 provided blue microcrystals (0.15g, 80%). Anal.(CHN) ^1H NMR 13.12(s,1H imine); 12.54(s,1H imine); 8.83(m,4H); 8.25(m,4H); 7.80(m,2H); 7.43(d, $J=9.44\text{Hz}$, 1H); 7.26(m,4H); 7.13(m,2H); 7.05(m,1H); 6.91(m,2H); 6.59(d, $J=8.25\text{Hz}$, 1H); 6.52 (d, $J=6.5\text{Hz}$, 1H); 5.23 (br,s,2H, amine); 4.74(br, s, 2H, amine).
16. Resonance Raman data are available in support of the assignments of the (RuQ.QRu) complex spectrum. Stufkens, D. J.; Lever, A. B. P. to be published.
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F.1

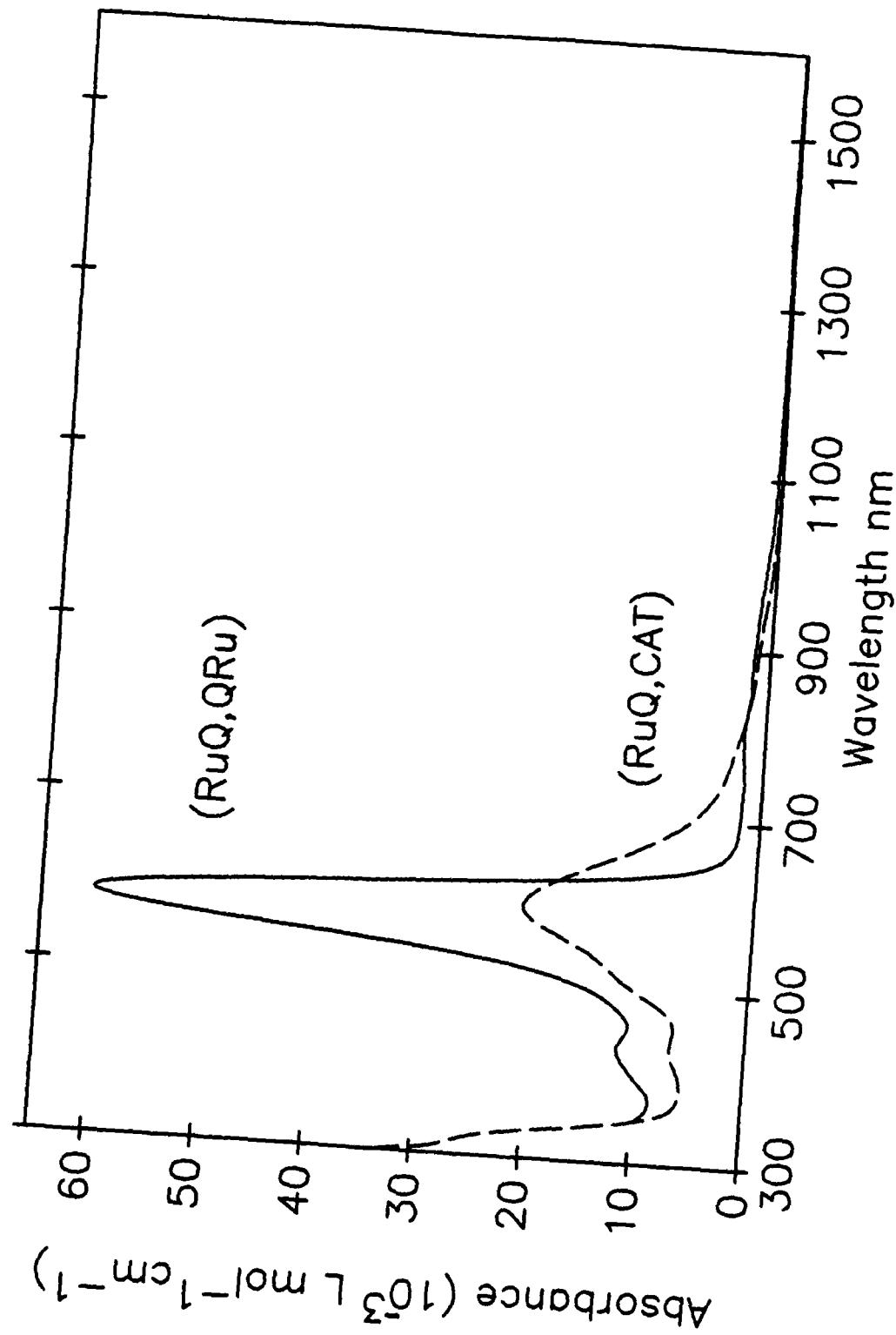


Fig. 2

